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PHOTOREACTION OF 6-HYDROXY-2,3-BENZOTROPONE

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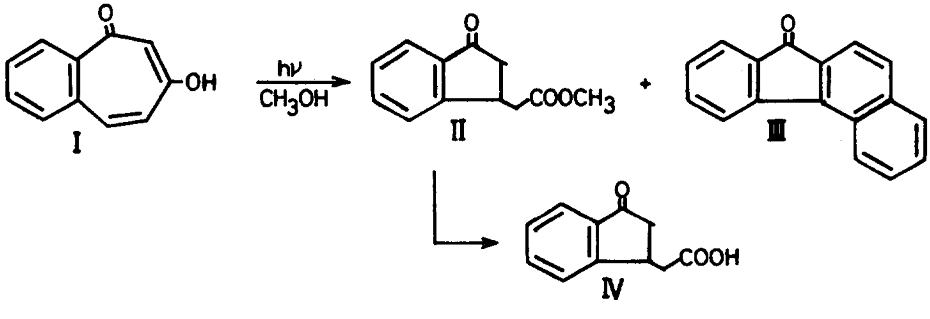
Recently, we have reported1) that 3,4-benzotropolone undergoes a novel type of photorearrangement to afford 1-hydroxy-6,7-benzobicyclo[3,2,0]hepta-3,6-dien-2-one. On the other hand, it was previously reported that, on irradiation, purpurogallin tetramethyl ether gave methyl 6,7,8-trimethoxy naphthoate2) and 4',5'-dimethoxy-3,4-benzotropolone methyl ether gave 1-methoxy-3,4-(4',5'-dimethoxy)benzobicyclo[3,2,0]hepta-3,6-dien-2-one.3) This remarkable difference on the photochemical behavior of 2,3-benzotropones according to their substituents prompted us to investigate further the photochemistry of 2,3-benzotropones. As 6-hydroxy-2,3-benzotropone (I) has a tautomeric structure 3-hydroxy-4,5-benzotropone, the photochemistry of I is of interest in connection with the photochemical results of 4,5-benzotropones.4)

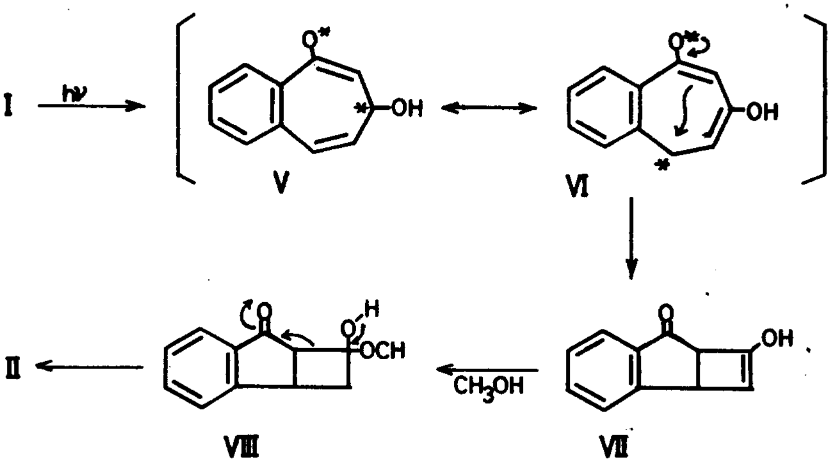
A dilute methanol solution of I was irradiated with pyrex filtered light under nitrogen atmosphere until the longest absorption maximum of I at 335 nm disappeared completely. By chromatographic separation of the reaction mixture, colorless oil (II), b.p. 60°(bath temperature)/5 mmHg, and orange prisms (III), m.p. 158-9°, were obtained in 25 % and 2 % yields, respectively, accompanied by several unidentified materials.



Compound III was identified as 3,4-benzofluorenone by comparison with an authentic sample prepared by the reaction of acetylanthranil with β-bromonaphthalene by the method described in the literature.5)

The structure of II was confirmed by the following spectral data, elemental analysis and chemical reaction. $\nu_{C=O}$(neat) 1730 and 1710 cm^{-1}. λ_{max}^{MeOH} 244 nm (log ε 4.2) and 286 nm (log ε 3.6). δ (60 MHz in $CDCl_3$) 7.85-7.22 (4H, aromatic) , 3.70 (3H, singlet, methyl), 4.05-3.75 (1H, broad, methine) and 3.25-2.19 (4H, complex absorption, methylene) ppm. m/e 204 (M^+), 173 (M^+-OCH_3), 145 ($M^+-COOCH_3$) and 131 ($M^+-CH_2COOCH_3$). Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 69.93; H, 5.98. An alkaline hydrolysis of II gave the corresponding acid as colorless prisms (IV), m.p. 152°. The assignment of the structure IV is consistent with the spectral characteristic [$\nu_{C=O}$(KBr) 1725 and 1680 cm^{-1}. λ_{max}^{MeOH} 244 nm (log ε 4.2) and 286 nm (log ε 3.6). δ (60 MHz in $CDCl_3$) 10.25 (1H, broad singlet, acid), 7.90-7.32 (4H, aromatic), 4.07-3.57 (1H, broad, methine) and 3.30-2.26 (4H, complex absorption, methylene) ppm] and elemental analysis [Calcd for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30. Found: C, 69.66; H, 5.38] of this compound.

It is well known that irradiation of 2- and 4-methoxy and/or hydroxytropones give rise to bicyclo[3,2,0]heptadienone compounds, however that of 3-methoxytropone does not afford a corresponding bicyclic compound because collapse of a excited state from 3-methoxytropone gives starting material rather than a bicyclic isomer.6) For mechanistic interpretation for formation of II from I, it will be assumed that a excited species VI is rather stable than a excited species V because of the presence of condensed benzene ring. Collapse of VI will afford a bicyclic compound VII. Reaction of VII with methanol will produce the compound II by the sequence (VII) → (VIII) → (II) in the same manner as the photoreaction of α-tropolone methyl ether in water to give methyl cyclopenta-2-en-1-onyl-4-acetate.6) The assumption of the presence of intermediary VII is supported by the fact that irradiation of 2,3-benzotropone7) gives 3,4-benzobicyclo[3,2,0]hepta-3,6-dien-2-one (IX) although irradiation of tropone8) results in the formation of several dimeric products



without giving a bicyclic compound. E. W. Collington and G. Jones isolated IX as oily material, b.p. 80°/0.02 mmHg, but we have obtained IX as colorless prisms, m.p. 37°, by purification by column chromatography on silica gel and then sublimation at 30°(bath temperature)/1 mmHg. $\nu_{C=O}^{KBr}$ 1710 cm^{-1}. λ_{max}^{MeOH} 248 nm (log ε 3.75) and 297 nm (log ε 3.20). δ (60 MHz in $CDCl_3$) 7.86-7.20 (4H, aromatic), 6.60 (1H, dd. J=2.5 and 0.6 Hz), 6.32 (1H, dd. J=2.5 and 1.5 Hz), 3.80 (1H, dd. J=2.6 and 1.5 Hz) and 4.35 (1H, dd. J=2.6 and 0.6 Hz) ppm.

The mechanism for the formation of III is the subject of further investigations.

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